The microscopic structure of adsorbed water on hydrophobic surfaces under ambient conditions

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Supporting Information

Methods and Supplementary Figures

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Methods

Preparation of the hydrophobic surfaces. *Hydrogen-terminated silicon(111) surfaces.* The substrates used were Sb-doped, *n*-type Si wafers with a low miscut angle of ±0.5° and a resistivity of 0.005-0.02 ohm·cm. Each Si wafer was cut into samples of approximately 1 cm × 1 cm. A standard RCA cleaning process was then carried out. Briefly, the substrates were immersed in a basic peroxide solution composed of 1:1:4 by volume of 28% $NH_3 \cdot H_2O$(aq)/30% H_2O_2/H_2O at 80°C for approximately 10 min, and then rinsed thoroughly in running Milli-Q water. H-terminated Si(111) surface was then formed after immersing the cleaned samples in 40% NH_4F for about 15 min. This procedure produces large, atomically flat terraces. *Trimethylchlorosilane (TMCS)-functionalized mica.* Mica surface functionalization was carried out through a vapor deposition process. Freshly cleaved muscovite mica (Grade V1; round disks of diameter 10 mm, Ted Pella) surfaces were first exposed to an environment with controlled relative humidity (RH) of 35±2% for about 5-10 min. The mica substrates were then quickly transferred into a sealed reaction vessel containing a beaker filled with ~5 ml of purified TMCS liquid and allowed to react for about 30-60 min. After TMCS-functionalization, the contact angle of the mica surface increased from ~0° to ~40°. *Graphite surfaces* were prepared by freshly peeling off the top few layers of graphite from a HOPG surface using Scotch tape.

Graphene templating of water adlayers on surfaces. Graphene sheets were prepared by the standard method of mechanical exfoliation (Novoselov *et al.* 2005; Lui *et al.* 2009) of Kish graphite onto the abovementioned surfaces. All experiments were performed at room temperature (22±2 °C). Humidity was monitored using a Fluke 971 temperature humidity meter. For graphene deposition at ambient conditions, the ambient RH was measured to be in a range of 36% to 42% for all experiments. The samples were allowed to equilibrate with the ambient environment for ~5 min before graphene was deposited. Low humidity (<3% RH) experiments were carried out in a glove-bag (Sigma-Aldrich AtmosBag) that was purged and protected under a continuous flow of ultra-high purity argon. The graphite surfaces were prepared inside the glove-bag and again allowed to equilibrate with the environment of controlled RH for ~5 min before graphene was deposited.

Identification of graphene layers. Graphene mono- and few-layers were identified through optical microscopy and confirmed by spatially resolved Raman spectroscopy. In the optical search process, we found it was easier to identify the thinnest graphene sheets on TMCS-functionalized mica using transmitted light (Fig. S1). For the basal planes of HOPG, we were able

to identify the edges of deposited graphene sheets through dark field scattering microscopy. In this mode, the contrast of the feature edges is enhanced (Fig. S1). For H-terminated Si(111) surfaces, we found the contrast of graphene sheets can be enhanced by proper filtering of the micrographs obtained from a CMOS camera (Fig. S1).

To confirm the identification of graphene layers on TMCS-functionalized mica and H-Si(111), spatially resolved Raman spectra were recorded. A Renishaw M1000 micro-Raman spectrometer system was used for this purpose using a 514.5 nm laser beam and a 2400 lines per mm grating. A confocal optical microscope with a ×100 objective lens was used to record spectra with a spatial resolution of 2 μm. As an example, Fig. S2 shows the representative Raman spectra for graphene deposited on the H-Si(111) surface. No noticeable D peak (~1350 cm^{-1}) was observed in the Raman spectra of the deposited graphene (Figs. S2), indicating high-crystalline order of our samples. The weak peak at ~1450 cm^{-1} is attributed to the third-order optical phonon mode of the silicon substrate (Temple and Hathaway 1973; Spizzirri 2010).

AFM Measurements. AFM images were acquired under tapping mode on a Digital Instrument Nanoscope IIIA at ambient conditions. A sharp TESP tip (Veeco) was used in the experiment. Typical values for the force constant, resonance frequency and tip radius were 42 N/m, 320 kHz, and 8 nm, respectively. Height calibrations were performed using the step heights of freshly cleaved graphite samples.

Supplementary Figures

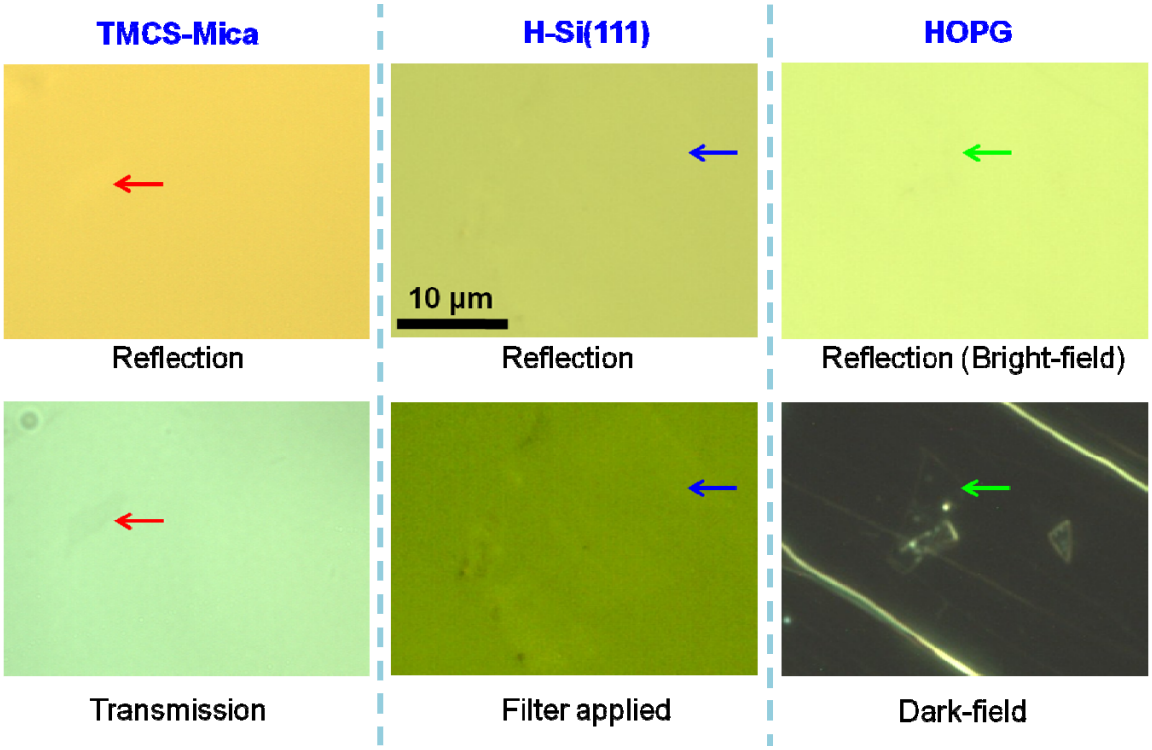

Fig. S1. Contrast enhancement/optimization for different substrates. Different optical imaging modes were used to facilitate the identification of graphene on the three hydrophobic surfaces investigated in this study. Under conventional, bright-field reflection optical microscope, none of the thinnest graphene sheets (arrows) were identifiable on the three surfaces. For TMCS-mica, the monolayer graphene can be readily identified by using transmitted light illuminations. For H-terminated Si(111) surfaces, the contrast of graphene sheets can be enhanced by proper filtering of the real-time micrographs obtained from a CMOS camera. For the basal planes of HOPG, enhanced edge contrast was achieved through dark field scattering microscopy. The result is that large-scale identification of deposited graphene was achieved for all three substrates. The scale bar (10 µm) applies for all images.

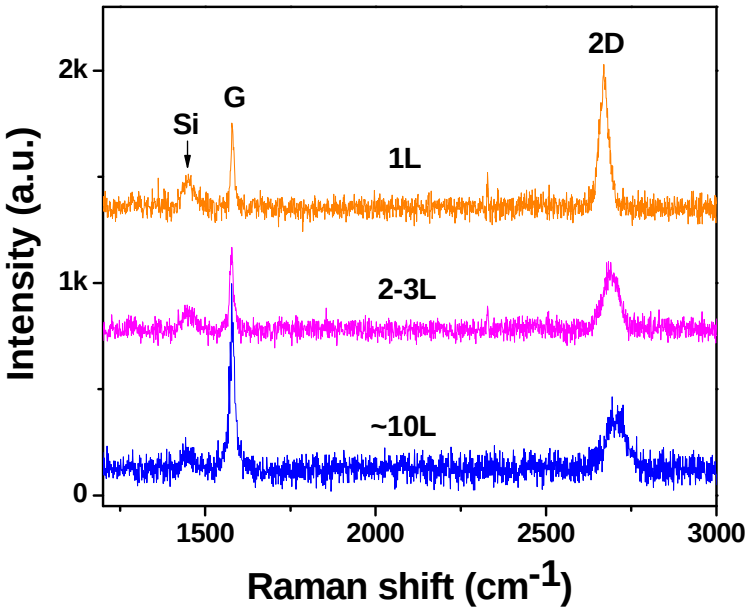

Fig. S2. Identification of numbers of graphene layers (labeled on each curve) for graphene deposited on the H-Si(111) surface. The monolayer curve was collected from the representative sample shown in Fig. S1. The 2-3 layer and ~10 layer data was taken from thicker graphene flakes deposited on the same wafer. No noticeable D peak (~1350 cm^{-1}) was observed in the Raman spectra, indicating high-crystalline order of graphene. The weak peak at ~1450 cm^{-1} is from the silicon substrate (3TO; third-order optical phonon mode of silicon).

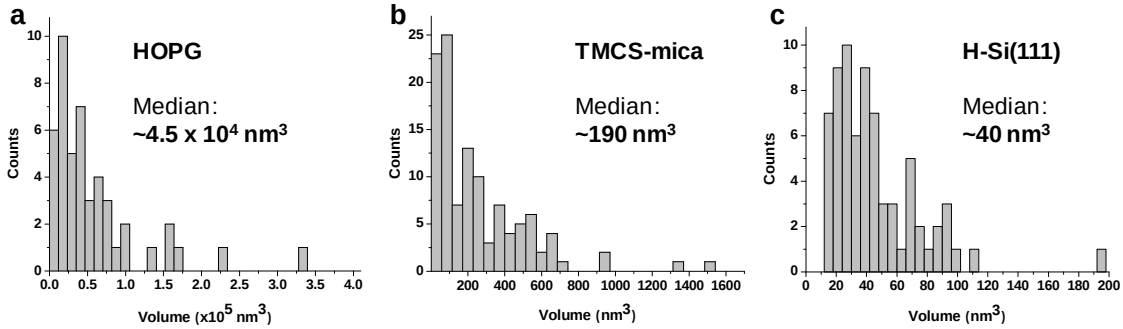

Fig. S3. Size distributions of the adsorbed nanodroplets. The volumes of the nanodroplets on the three surfaces were obtained by numerical integration, with background subtracted. The median values of the nanodroplet volumes for the three surfaces are indicated in the plots.

References

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